

Laboratory Study of Heterogeneous Reactions of Calcium Carbonate in an Environmental Aerosol Chamber

Amy Preszler Prince, Paul Kleiber,
Mark Young and Vicki Grassian

University of Iowa
Department of Chemistry
Center for Global and Regional Environmental Research (CGRER)
Iowa City, Iowa



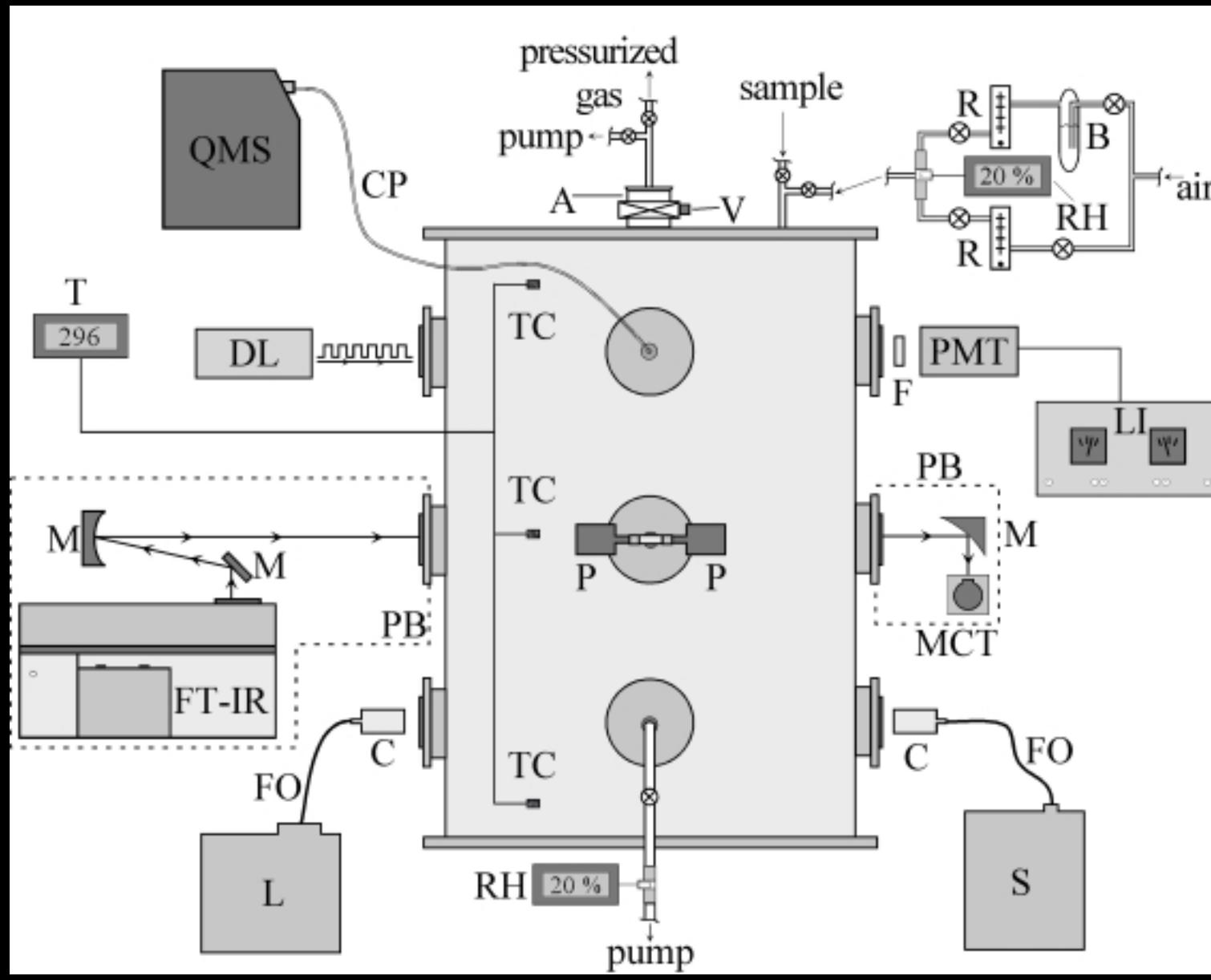
Heterogeneous Reactions of HNO₃ and SO₂ with Calcite

- HNO₃ and SO₂ are important tropospheric species ¹
 - Acid rain
 - CCN (reaction with ammonia to form ammonium salts)
 - Photochemical oxidant cycle
- In the presence of water, nitric acid and calcite will react: ^{2,3}
$$2\text{HNO}_3\text{(g)} + \text{CaCO}_3\text{(s)} \longrightarrow \text{Ca}(\text{NO}_3)_2\text{(s)} + \text{CO}_2\text{(g)} + \text{H}_2\text{O(g)}$$
- In the atmosphere, sulfur dioxide and calcite will react forming ^{4,5}
 - calcium sulfite hemihydrate ($\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$)
 - gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)

Important Considerations

- Reactivity dependence of calcite aerosol at varying relative humidities (RH) with HNO_3 and SO_2
- Possible formation of gas-phase products and surface adsorbed species
- Stoichiometric limitation: surface or bulk limited
- Chemical processing - after reaction with HNO_3 or SO_2
 - Further reaction of adsorbed species
 - Site blocking
 - Enhanced reactivity

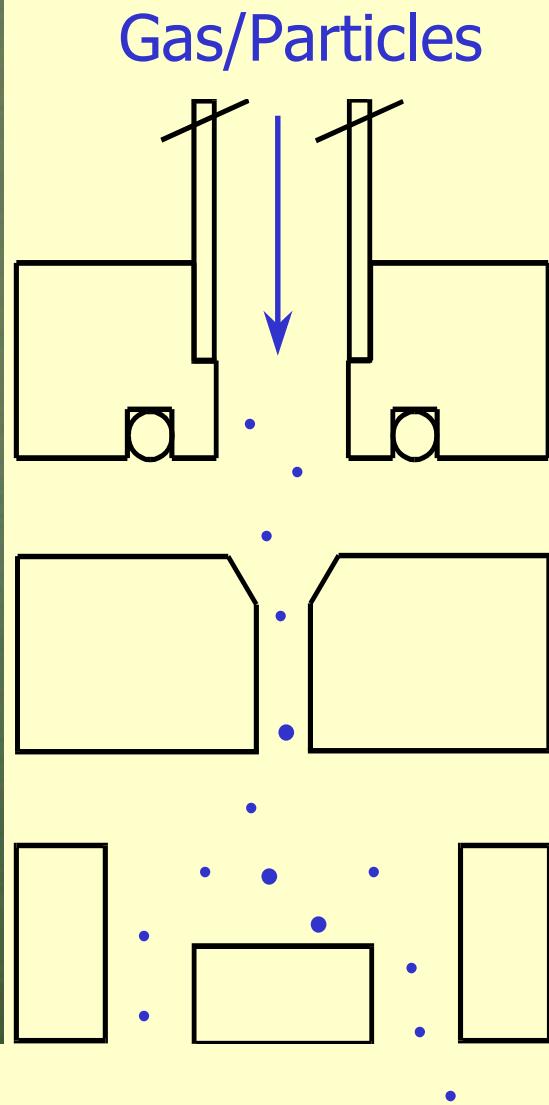
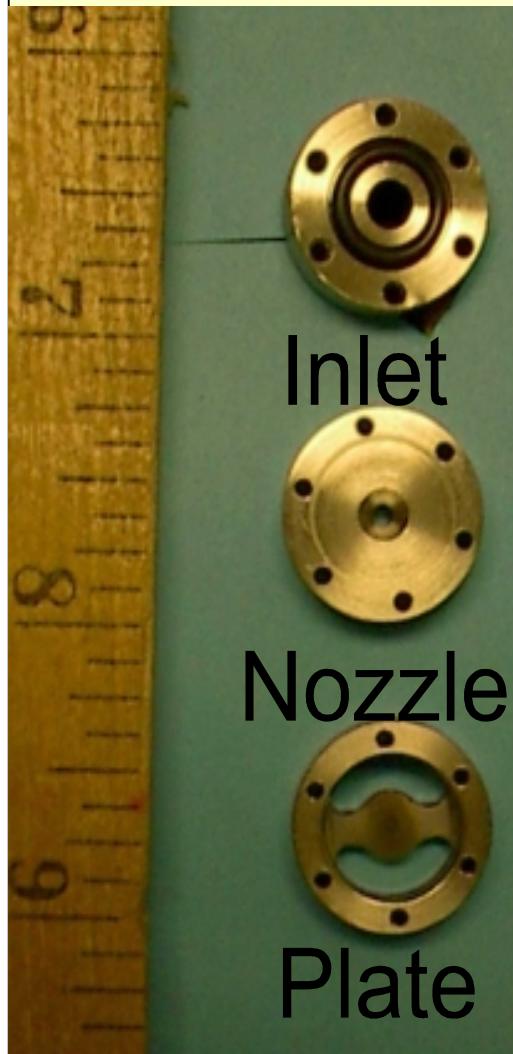
Experimental Schematic



Methodology

- Evacuate chamber
- Prepare powder sample for injection
- Add reagent gas and humidity controlled matrix gas
- Characterize background
- Generate aerosol
- Spectroscopically monitor decay/growth of gas phase and adsorbed species

Partial Impactor



Experimental Parameters

Aerosol: CaCO_3

- OMYA UF Calcite
- \bar{D}_P 0.6 μm
- BET Surface Area
10.1 m^2/g
- Mass Loading
 $\sim 4 \text{ g/m}^3$

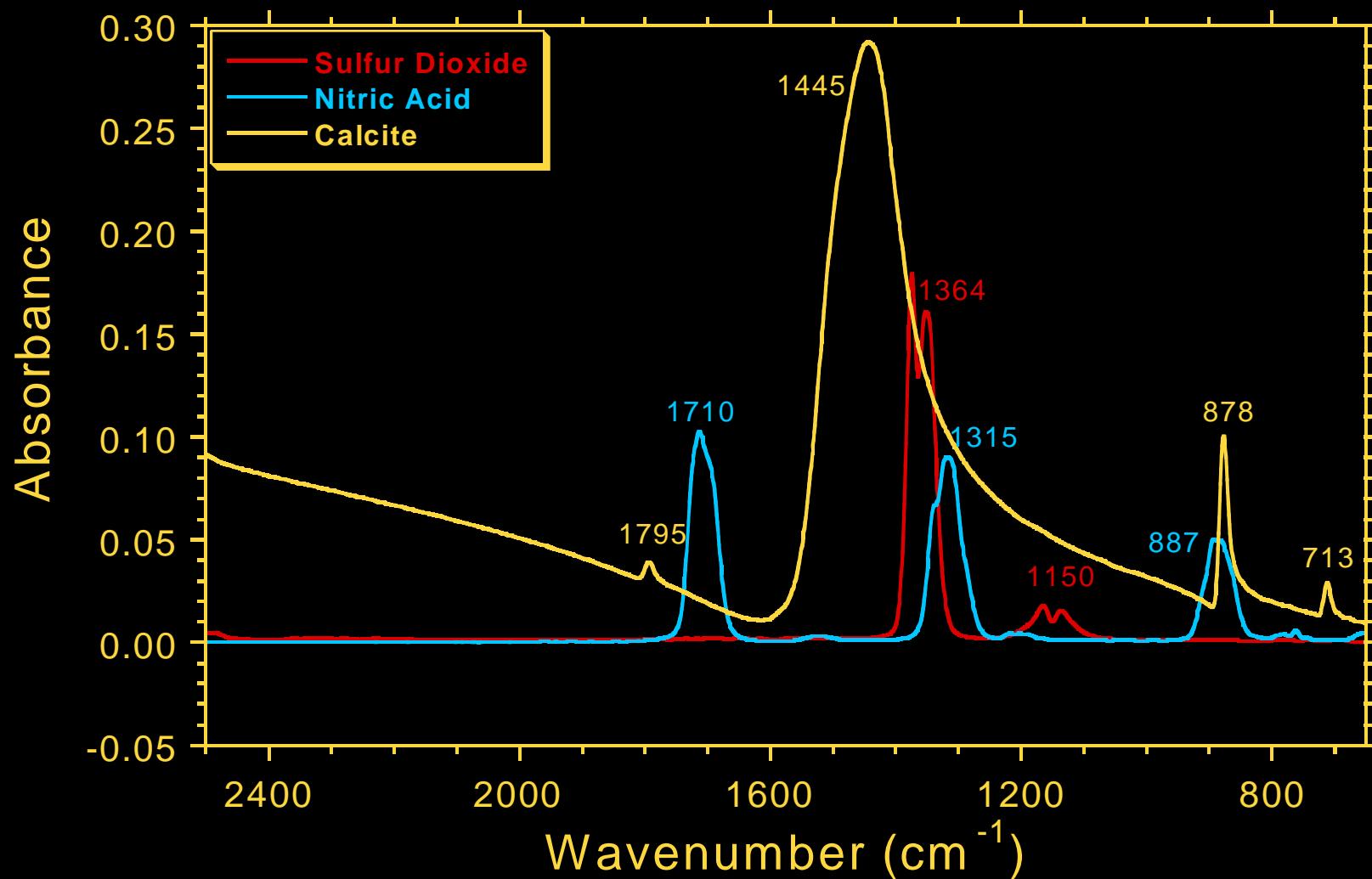
Reagent Gas: HNO_3

- Pressures: 6 - 600 mTorr
- RH (purge - 40%RH)
- Total Pressure 778 Torr

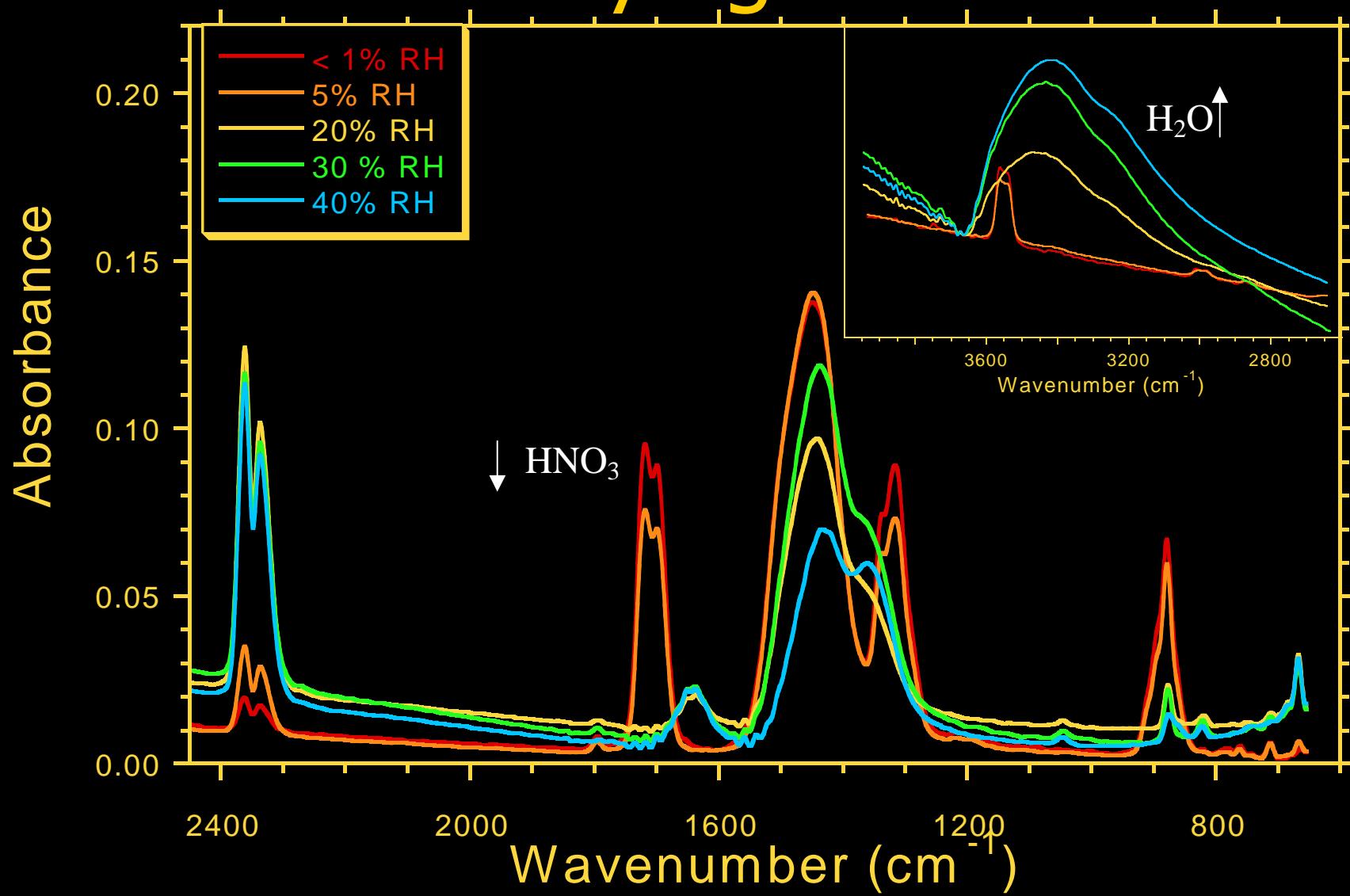
Reagent Gas: SO_2

- Pressure: 360 mTorr
- RH (purge - 89%)
- Total Pressure 778 Torr

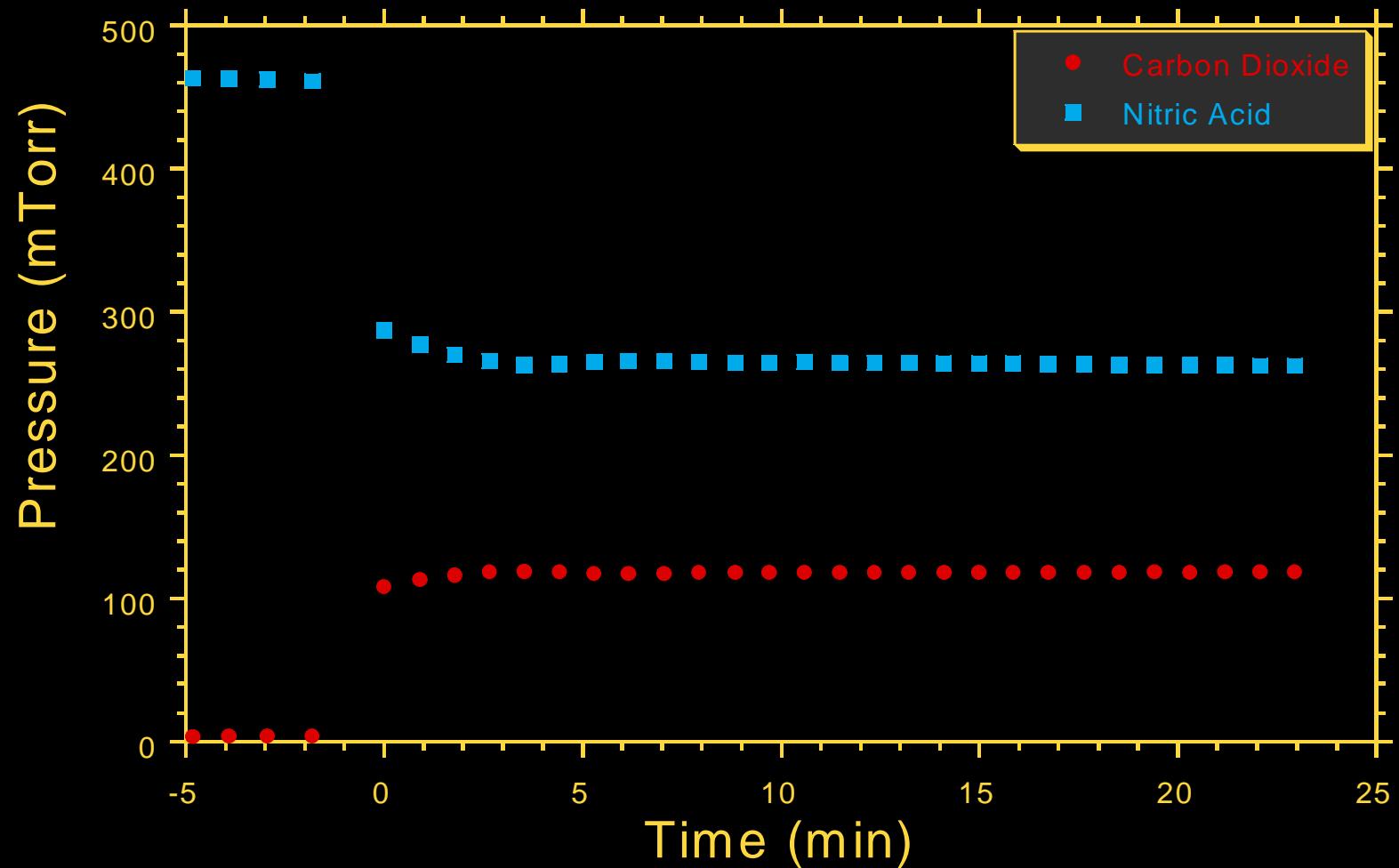
IR Spectra: CaCO_3 , HNO_3 , SO_2



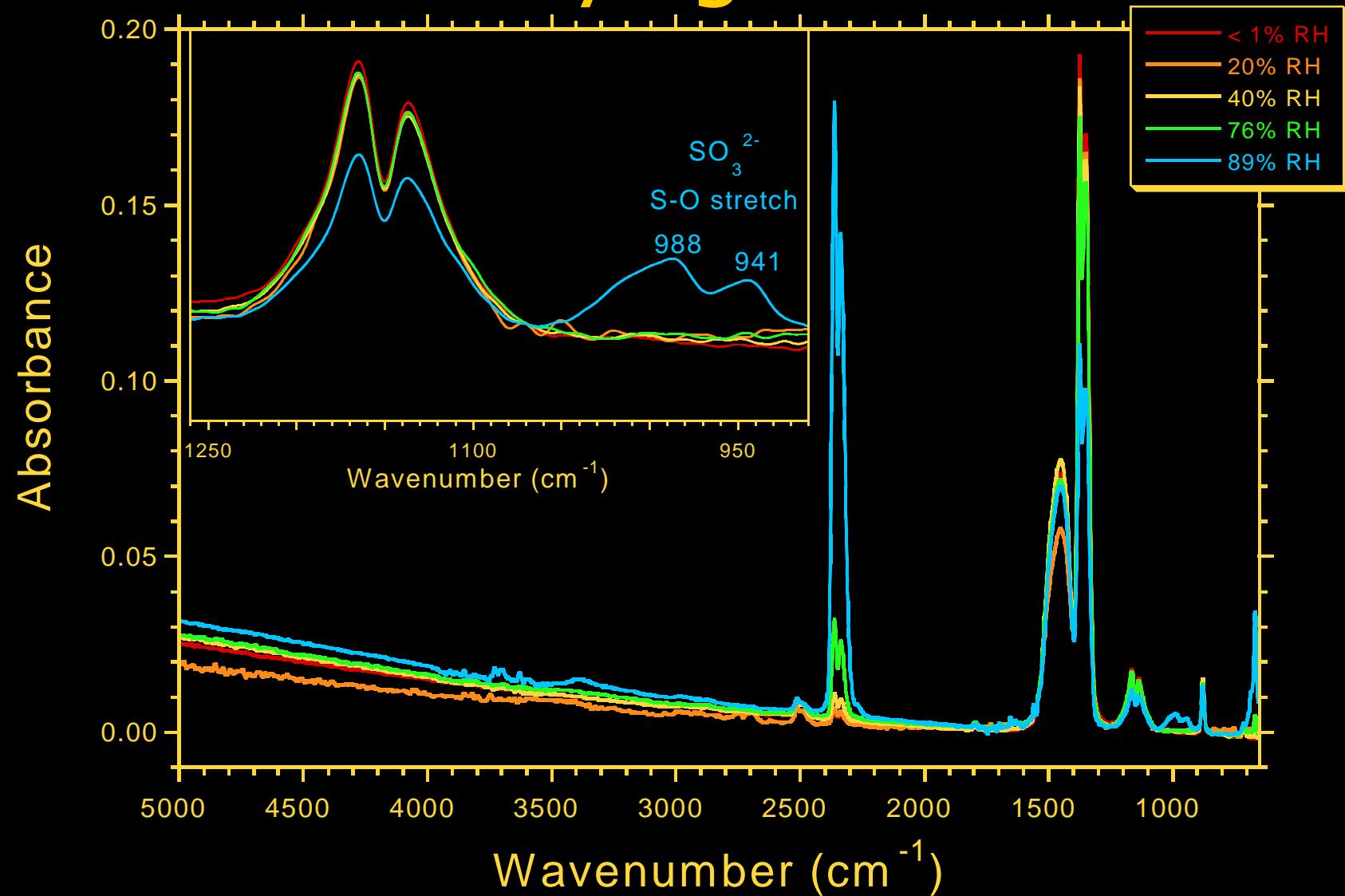
IR Spectra: HNO_3 and Calcite at Varying % RH



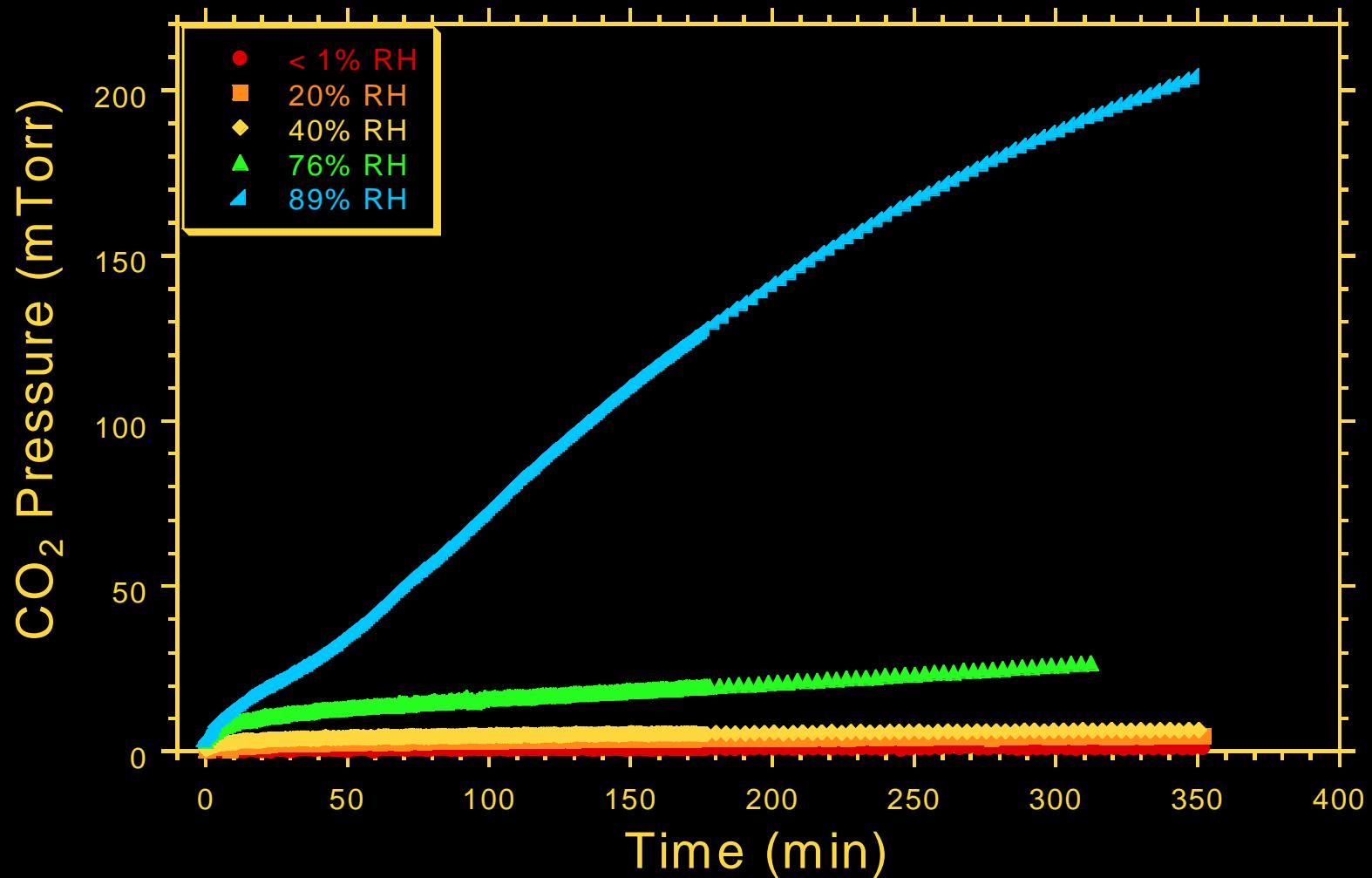
HNO_3 Loss and CO_2 Production



IR Spectra: SO_2 and Calcite at Varying % RH



Reaction of SO_2 and CaCO_3 : CO_2 Production



SO_2 Loss vs CO_2 Production

% RH	CO_2 (mTorr) produced	SO_2 (mTorr) reacted	$\text{SO}_2:\text{CO}_2$
Purge	1.0	-	-
19	3.9	0.9	0.2
40	5.9	7.5	1.3
76	22	22	1.0
89	148	161	1.1

Summary: HNO₃/CaCO₃

- HNO₃/CaCO₃ reaction is stoichiometric

- 2:1 HNO₃ loss : CO₂ production



- Observed adsorbed species

- Nitrate, water

- Increased adsorption of water after reaction with nitric acid

- Conversion of CaCO₃ to Ca(NO₃)₂ increases water adsorption
 - Changes in particle size

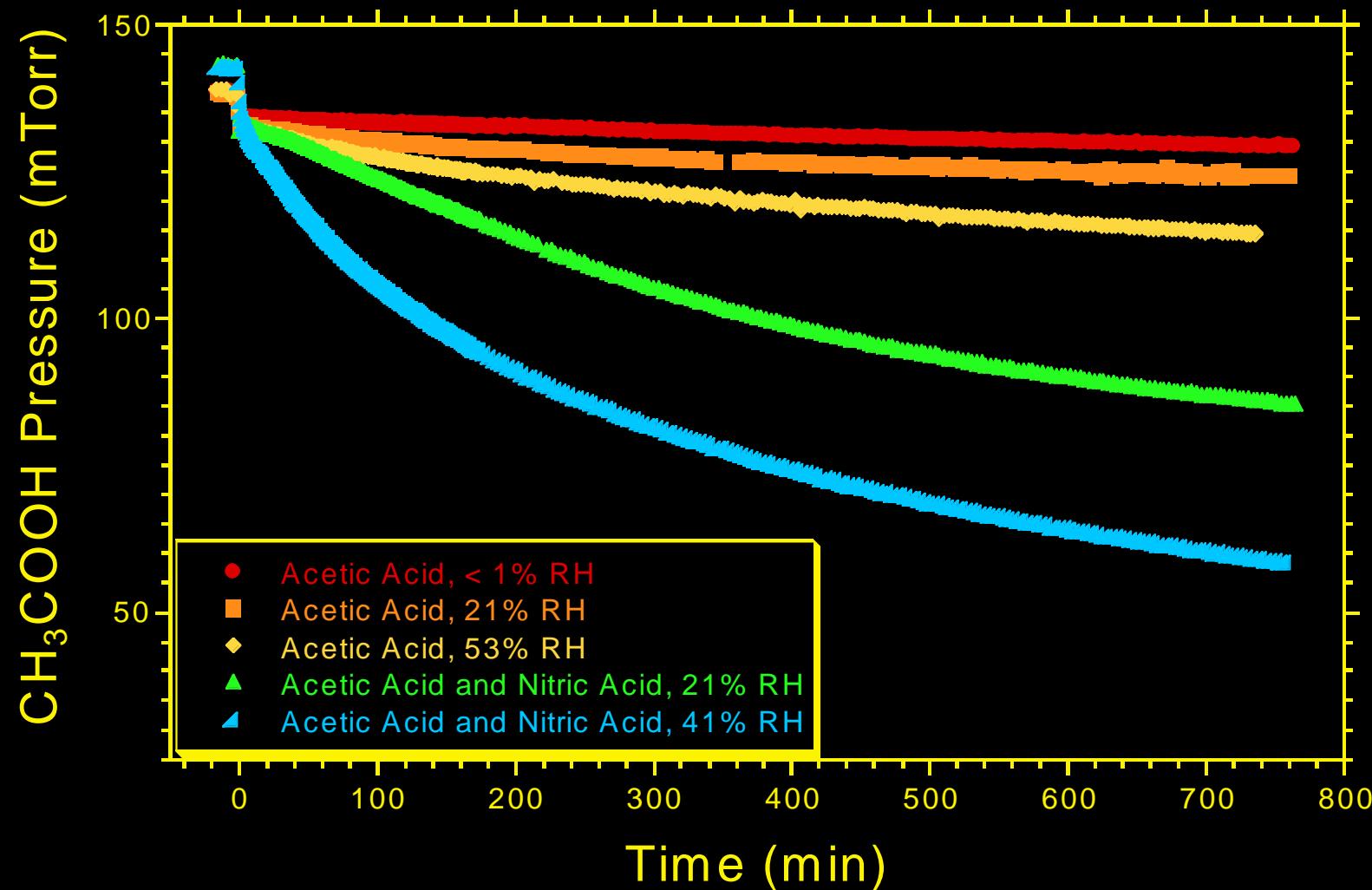
- Reaction into bulk, not surface limited

- Enhanced uptake of nitric acid with increased relative humidity

- Enhanced acetic acid uptake kinetics in the presence of nitric acid

Reactions of Organic Acids with Calcite

Kinetic Data: $\text{CaCO}_3 + \text{CH}_3\text{COOH}$



Summary: SO₂/CaCO₃

- CO₂ production increased with increasing RH in CaCO₃/SO₂ system



- At ~ 90% RH observed formation of sulfite, increased CO₂ production and increased SO₂ uptake
- Future experiments to determine if SO₂ uptake will be effected by physicochemical changes in the aerosol particle
 - Quantify RH dependence
 - Aged and processed particles (nitrate coated)
 - Kinetic competition reactions (HNO₃ and SO₂)

References

- 1) Seinfeld, J. H.; Pandis, S. N.; *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, Wiley: New York, 1998.
- 2) A. Goodman, G. Underwood, V. Grassian; "A laboratory study of the heterogeneous reaction of nitric acid on calcium carbonate particles"; *J. Geo. Res.* 105 (D23) (2000) 29053-29064.
- 3) F. Fenter, F. Caloz, M. Rossi; "Experimental evidence for the efficient "dry deposition" of nitric acid on calcite"; *Atm. Envir.*; 29 (22) (1995), 3365-3372.
- 4) H. Böke, E. H. Göktürk, E. N. Caner-Saltik, Ş. Demirci; "Effect of airborne particle on SO₂-calcite reaction"; *App. Sur. Sci.*; 140 (1999) 70-82.
- 5) P. Elfving, I. Panas, O. Lindqvist; "Model study of the first steps in the deterioration of calcareous stone I. Initial surface sulphite formation on calcite"; *App. Sur. Sci.*; 74 (1994) 91-98.